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SERIES IN THE ARC SPECTRUM OF MOLYBDENUM.

By C. C. Kiess.

ABSTRACT.

Many of the strong lines of the arc spectrum of molybdenum have been found to be members of series. These are of several types. Narrow triplets characterized by the frequency differences 121.5 and 87.0 have been arranged into the series $1S-mP_i$, $2P_i-mS$, and $2P_i-mD$. Widely separated triplets, between which the frequency differences 448.5 and 257.5 exist, form the series $1s-mp_i$, $2p_i-ms$, and $2p_i-md_j$. Parallel to these wide triplet series are other series $1s-(mp_i+k_i)$, $(2p_i-k_i)-ms$ and $(2p_i-k_i)-md_j$, of which the separations 379.9 and 233.4 are characteristic. The limits of these series have been calculated with formulas of the Ritz type and with the aid of the interseries combination lines $1s-2P_2$, $1s-2P_3$, $1S-2p_2$, and $1S-2p_3$. From the known values of $1s$ and $2p_1$ it follows that the resonance and ionization potentials of molybdenum are 3.25 volts and 7.35 volts, respectively. In addition to the triplets there occur in the spectrum of molybdenum groups of 9, 10, and 13 lines known as multiplets, which arise from the combinations of the various threefold and fivefold levels which exist beyond the $1s$ level of the atom.

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I. INTRODUCTION.

The arc spectrum of molybdenum has been measured from wave length 2300 A in the ultra-violet to the neighborhood of 9700 A in the infra-red. The literature describing the earlier work on the spectrum of this element is reviewed in Kayser's Handbuch, vol. 5. In recent years new measurements of the spectrum have been made expressing the wave lengths in international units. The work of Frl. Puhlmann[1] describes the spectrum from 2420 A to 4888 A. From 4647 A to 7134 A the spectrum has been measured by Weigand,[2] and from 5501 A to 9721 A wave-length data have

[1] Zeit. für Wiss. Phot., **17**, p. 97; 1917.

[2] Zeit. für Wiss. Phot., **11**, p. 261; 1912.

been published by Kiess and Meggers.[3] The work of all these observers shows the spectrum to be exceedingly rich in lines, most of which are of a low order of intensity.

The series regularities in the arc spectrum of molybdenum, which it is the purpose of this paper to describe, were found as a result of a similar investigation made of the spectrum of chromium. Because of its relationship to chromium, in the periodic classification of the elements, series structures similar to those of chromium are to be expected in the spectrum of molybdenum. For chromium[4] three systems of series, whose members are triplets, have been established, each system being composed of principal, sharp, and diffuse series. In two of the systems, those characterized by widely separated triplets, the component series are parallel; that is, homologous members of each series are separated by constant wave-number differences. The third system of series, composed of narrow triplets, corresponds to the singlet series of the alkaline earths.

Regularities in the spectrum of molybdenum have already been pointed out by Paulson,[5] and also by Kiess and Meggers.[6] These consist for the most part of pairs of lines between which constant frequency differences exist. As will be shown later, nearly all such pairs are members of series regularities.

II. OBSERVATIONS.

To aid in the visual examination of the spectrum a set of spectrograms extending from 2300 A to 6100 A was made with a concave grating ruled 20,000 lines per inch. In addition to these large-scale photographs there were available for use the lower-dispersion plates extending from 5500 A to 9700 A, upon which the previously mentioned work of Kiess and Meggers was based. Such a set of spectrograms is an invaluable aid in indicating what groups of lines may serve as a starting point in unraveling series and other regularities. Some of these plates have been partially measured to check the published values of wave lengths and intensities; but with few exceptions, which will be indicated in the following tables by marking the lines in question with an asterisk (*), all the wave-length data given in this paper are taken from the sources mentioned above.

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[3] B. S. Sci. Papers, **16**, p. 61; 1920.
[4] Science, **56**, p. 666; 1922; Compt. Rend., **176**, p. 84; 1923.
[5] Dissertation, Lund, 1914; also Astrophys, Jl., **40**, p. 302; 1914
[6] B. S. Sci. Papers, **16**, p. 61; 1920.

III. THE NARROW-TRIPLET SERIES.

A prominent feature of the greenish-yellow region of the spectrum of molybdenum is the triplet at 5506 A, 5533 A, and 5570 A. The lines of this triplet are separated by the frequency differences $\Delta\nu_1 = 121.47$ and $\Delta\nu_2 = 86.96$. Associated with this triplet is another in the infra-red at 8245 A, 8328 A, and 8389 A and characterized by the same frequency differences. A systematic search through a table of wave numbers prepared from the published wave lengths revealed several more triplets of this type, and from them have been arranged the series presented in Table 1. The series constants have been calculated with a formula of the Ritz type, namely:

$$\nu_m = L - \frac{N}{\left(m + a + \frac{b}{m^2}\right)^2}$$

in which $N = 109678.3$, the value recently published by Curtis.[7] The corrections applied to the wave lengths in air to reduce them to vacuum values have been taken from the tables of Meggers and Peters.[8]

The above formula applied to the first lines of the triplets of the sharp series gives:

$$\nu_m = 30845.29 - \frac{109678.3}{\left(m + 0.393671 + \frac{0.105617}{m^2}\right)^2}$$

where $m = 1, 2, 3, \ldots$.

The remaining two limits, found by subtracting, successively, the triplet separations 121.48 and 86.95 from the above value for $2P_1 = 30845.29$, are, respectively, $2P_2 = 30723.81$ and $2P_3 = 30636.86$.

Of particular interest is the fact that the triplets of the principal, sharp, and diffuse series are arranged in the reverse order from what has been observed hitherto in triplet series; and, furthermore, the first lines of the triplets are of lower intensity than the other two. The diffuse triplet resembles the type already found in the widely separated triplets of chromium and manganese; that is, each component is itself a narrow triplet, indicating that the D term which combines with $2P_i$ is fivefold.

In the spectra of the elements of column 2 of the Periodic Classification occur singlet and triplet series. It is believed that

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[7] Proc. Roy. Soc., A. **96**, p. 147; 1919.

[8] B. S. Bulletin, **14**, p. 731; 1918.

the narrow triplet series of chromium and molybdenum are analogous to the singlet series of the alkaline earths and associated elements. For this reason the letters *S*, *P*, and *D* have been chosen to designate the narrow triplet series. A similar plan has been adopted by Catalán for designating the narrow triplet series of manganese.

IV. THE PARALLEL SERIES OF WIDE TRIPLETS.

According to de Gramont,[9] the three lines at 3798 A, 3864 A, and 3903 A constitute the *raies ultimes* of molybdenum. Each line of this triplet in the arc spectrum of molybdenum is very intense and self-reversed. For all elements for which series relationships have been established the *raies ultimes* are the resonance lines and in most cases they are the first members of the principal series.[10] The frequency differences characterizing this triplet are $\Delta\nu_1 = 448.62$ and $\Delta\nu_2 = 257.51$. Triplets with the same separations and corresponding to the first members of the sharp and diffuse series have been found in the extreme red and in the green spectral regions, respectively. The diffuse triplet has the same structure as has been found for the diffuse triplets of chromium [11] and of manganese.[12] That is, instead of being composed of six lines, as in the diffuse triplets of the alkaline earths, the diffuse triplet of molybdenum is composed of nine lines, each compenent of the triplet being itself a narrow triplet.

In the ultra-violet lies a second triplet of intense, self-reversed lines, between the components of which the frequency differences $\Delta\nu_1 = 379.90$ and $\Delta\nu_2 = 233.42$ exist. The differences between the wave numbers of this triplet and those of the *raies ultimes* are 5592.87, 5661.59 and 5685.68, respectively. Applying these numbers to the wave numbers of the lines of the green, diffuse triplet we find in the extreme red a second diffuse triplet characterized by the frequency differences 379.90 and 233.40. The sharp triplet, which might also be expected, falls in the infra-red and has not yet been observed. Thus, it is seen that, as in chromium, the two types of widely separated triplets are members of parallel systems of series, any line of a given series being separated from a corresponding line in a parallel series by a constant amount.

[9] Compt. Rend., **171**, p. 1106: 1920.

[10] Compt. Rend., **175**, p. 1027: 1922.

[11] Science, **56**, p. 666: also Compt. Rend., **176**, p. 84; 1923.

[12] Phil. Trans. Roy. Soc. London, **A223**, p. 133; 1922.

Table 2 lists the members that have been found for the different series of the two parallel series systems of widely separated triplets. The Ritz equation for the first lines of the sharp series is:

$$\nu_m = 33239.94 - \frac{109678.3}{\left(m + 0.345725 + \frac{0.011281}{m^2}\right)^2}$$

where $m = 1, 2, 3, \cdots$

The value taken for the limit $2p_1 = 33239.94$ was calculated from the value $2P_1 = 30845.29$, as found from the narrow triplets, and from the interseries combination lines which are discussed in the following section.

TABLE 1.—Series of Narrow Triplets of Molybdenum.

Principal series, 1S—mP. 1S=48792.17.

λ I. A.	Int.	ν vacuum.	Δ ν	m	mP_i
5570.46	25R	17946.88	121.47	2	30845.29
5533.01	30R	18068.36	86.96		30723.81
5506.51	40R	18155.31			30636.86

Sharp series, $2P_i$—mS. $2P_1$=30845.29; $2P_2$=30723.81; $2P_3$=30636.86.

λ I. A.	Int.	ν vacuum.	Δ ν	m	mS
−5570.46	25R	−17946.88	121.47	1	48792.17
−5533.01	30R	−18068.36	86.96		
−5506.51	40R	−18155.31			
8245.06	3	12125.15	121.37	2	18720.11
8328.43	5	12003.78	87.07		
8389.28	6	11916.71			
4673.78	1	21390.01	121.56	3	9455.32
4700.49	2	21268.45	86.91		
4719.77	2	21181.54			

Diffuse series, $2P_i$—mD. $2P_1$=30845.29; $2P_2$=30723.81, $2P_3$=30636.86.

λ I. A.	Int.	ν vacuum.	Δ ν	m	mD_i
5848.82	2	17092.73	2.68		
5849.72	3	17090.05	5.21	3	
5851.52	3	17084.84			
			121.34		
5891.60	2	16968.62	5.12		13752.56
5893.38	3	16963.50	7.13		13755.18
[1] 5895.86	5	16956.37			13760.39
			87.06		13767.57
5923.78	1	16876.44	7.28		13774.76
5926.34	4	16869.16	7.06		
5928.82	7	16862.10			

[1] The line 5895.86 is not given in the tables of Weigand nor in those of Kiess and Meggers. It was apparently omitted in the belief that it was the D_1 line of Na. A spectrogram recently made at the Bureau of Standards with very pure molybdenum shows this line prominently while D_2, if present at all, is very faint.

TABLE 2.—Parallel Series of Wide Triplets of Molybdenum.

Principal series, 1s—mpᵢ. 1s=59560.37.						Principal series, 1s—(mpᵢ+k).					
λ I. A.	Int.	ν vacuum.	Δ ν	m	mpᵢ	λ I. A.	Int.	ν vacuum.	Δ ν	m	Separation k
3798.26	50R	26320.43	448.62	2	33239.94	3132.59	10R	31913.30	379.90	2	5592.87
3864.12	50R	25871.81	257.51		33688.56	3170.33	10R	31533.40	233.42		5661.59
3902.97	50R	25614.30			33946.07	3193.97	10R	31299.98			5685.68

Sharp series, $2p_i-ms$. $2p_1=33239.94$; $2p_2=33688.56$; $2p_3=33946.07$.						Sharp series, $(2p_i-k_i)-ms$.					
λ I. A.	Int.	ν vacuum.	Δ ν	m	ms	λ I. A.	Int.	ν vacuum.	Δ ν	m	Separation k
—3798.26	50R	—26320.43	448.62	1	59560.37	—3132.59	10R	—31913.30	379.90	1	5592.87
—3864.12	50R	—25871.81	257.51			—3170.33	10R	—31533.40	233.42		5661.59
—3902.97	50R	—25614.30				—3193.97	10R	—31299.98			5685.68
7485.73	7	13355.10	448.42	2	19884.95						
7242.54	7	13803.52	257.58								
7109.87	8	14061.10									

Diffuse series, $2p_i-md_j$. $2p_1=33239.94$; $2p_2=33688.56$; $2p_3=33946.07$.						Diffuse series $(2p_i-k_i)-md_j$.					
λ I. A.	Int.	ν vacuum.	Δ ν	m	mdᵢ	λ I. A.	Int.	ν vacuum.	Δ ν	m	Separation k
5367.01	2	18627.18	9.51	3		7670.02*	<1	13034.19	9.83	3	5592.99
5364.27	3	18636.69	12.79			7664.24	1	13044.02	12.79		5592.67
5360.59	15	18649.48			14590.46	7656.74	4	13056.81			5592.67
			448.31		14603.26				379.84		
5242.78	3	19068.58	6.91		14613.09	7456.65	1	13407.16	6.87		5661.42
5240.88	5	19075.49	9.79		14620.03	7452.83	2	13414.03	9.96		5661.46
5238.19	5	19085.28			14624.71	7447.30	2	13423.99			5661.29
			257.15						233.41		
5174.18	7	19321.36	4.63			7331.51	2h	13636.02	4.67		5685.34
5172.94	8	19325.99	6.65			7329.00	2h	13640.69	6.75		5685.30
5171.16	7	19332.64				7325.37	1	13647.44			5685.20

V. THE INTERSERIES COMBINATION LINES.

Lines which represent combinations between the S and p_i terms and also the s and P_i terms have been recognized in those given in Table 3.

TABLE 3.—Interseries Combination Lines.

Designation.	λ I. A.	Int.	ν vacuum.	Δν
$1S-2p_2$	6619.16	8	15103.51	257.50
$1S-2p_3$	6733.97	6	14846.01	
$1S-(2p_2+k_2)$	4814.47	3	20764.94	233.34
$1S-(2p_3+k_3)$	4869.19	3	20531.60	
$1s-2P_2$	3466.83	8	28836.56	87.08
$1s-2P_3$	3456.39	10	28923.64	
$2p_1-2S$	6898.02	2	14492.92	448.33
$2p_2-2S$	6691.04	2	14941.25	
$2s-2P_1$	9123.83	1	10957.30	....

From the limit of the sharp series of narrow triplets we have $2P_2 = 30723.81$. Combining this with the observed value of $1s-2P_2$ there results the value $1s = 59560.37$, which is the convergence frequency of the principal series of wide triplets. Applying the Rydberg-Schuster rule, we find for the limit of the sharp series of wide triplets $2p_1 = 59560.37 - 26320.43 = 33239.94$.

VI. THE RESONANCE AND IONIZATION POTENTIALS.

From the series data just presented it is seen that, in the neutral state, the valence electron of molybdenum occupies the $1s$ orbit. To remove this electron to some outer orbit, the atom must absorb energy[13] in the amount $h\ c/\lambda = e\ V$, in which λ is the wave length of the light emitted on the return of the electron to its normal position. By means of this relation we may calculate the resonance and ionization potentials of molybdenum. When the proper values are assigned to the constants involved we have $V = 1.234/\lambda$. Hence, for the line $1s-2p_1$, which is the resonance line of molybdenum, we find that the resonance potential should be $V_R = \frac{1.234}{0.379826} = 3.25$ volts. For the ionization potential we use the limit of the principal series converging at $1s$. Therefore, this potential should be $V_I = 1.234 \times 1s \times 10^{-4} = 7.35$ volts.

VII. THE ENERGY DIAGRAM.

It is instructive to illustrate diagramatically, as in Figure 1, the distribution of the various orbits involved in the emission of the series lines just described. According to modern theories light is emitted by an excited atom when the valence electron springs from an outer orbit to an inner one. In the unexcited state the electron occupies the $1s$ orbit which has the term value 59560, which is a measure of the energy of the atom when prefixed with the negative sign. The resonance lines are emitted when the electron in the excited atom returns from the triple $2p$ level to $1s$. The wave numbers of the emitted light waves are equivalent to the lengths of the arrows joining $2p_i$ with $1s$, which are equal to the differences between the terms, namely, $1s-2p_i$. Associated with the $2p_i$ level is another threefold level $2p'_i$. It is the transitions between these two sets of levels which give rise to the lines of the two parallel systems of series of widely separated triplets. Of particular interest is the $3d_i$ level, which

[13] Sommerfeld, Atombau, 3d Ed., p. 418; 1922.

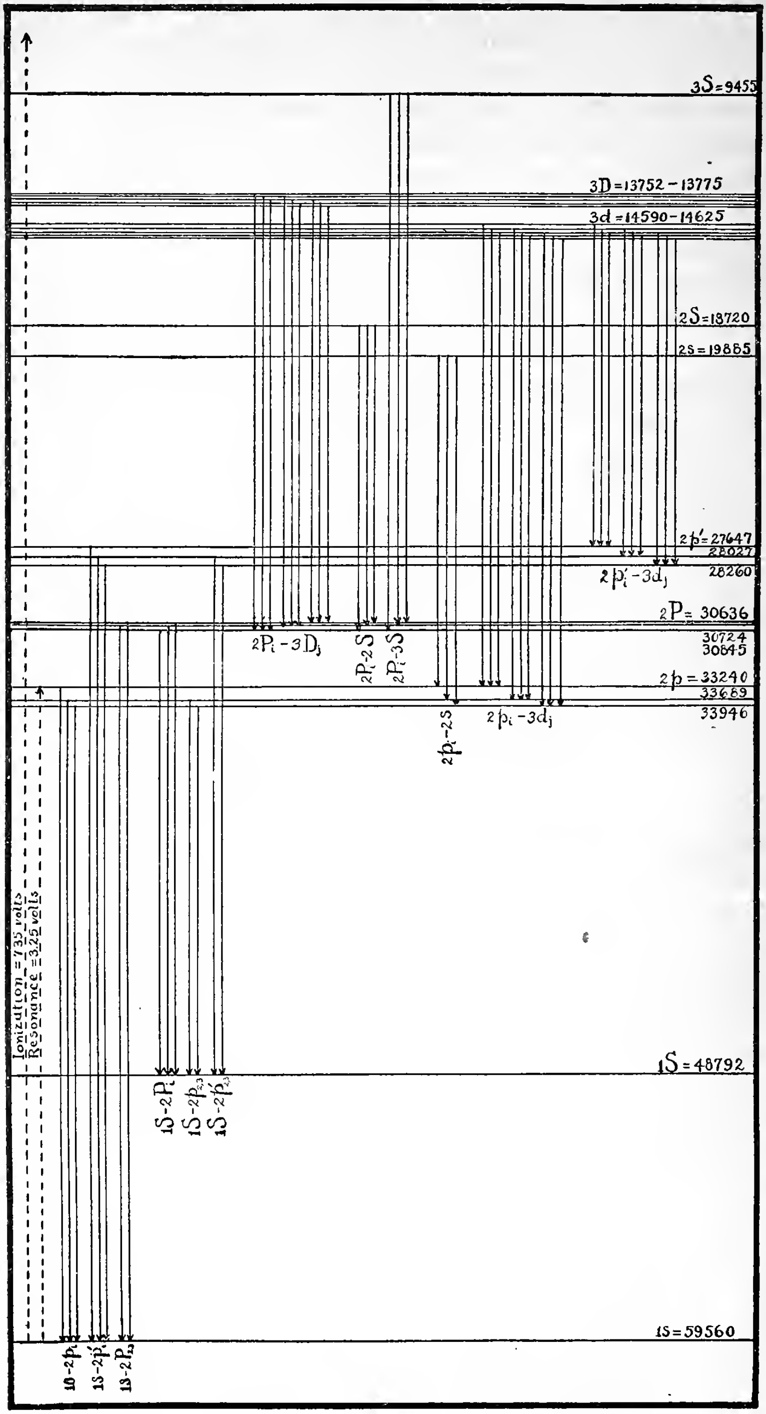

FIG. 1.—*Energy diagram of the series triplets of molybdenum.*

is fivefold. The permissible transitions between it and the $2p_i$ and $2p'_i$ levels give rise to the two diffuse triplets of which each component is itself a narrow triplet.

A second set of levels, analogous to those giving rise to the singlet series of the alkaline earths, also exists. In molybdenum, however, the $2P$ level is triple instead of single, and therefore the combinations between it and the mS and multiple mD levels give rise to triplets and nonets. The frequency with which the levels $2P_2$ and $2P_3$ enter the various combinations is greater than for $2P_1$, as is evidenced by the fact that the intensities of the second and third lines of the triplets $2P_i-mS$ and $2P_i-mD$ are greater than the intensities of the first lines.

VIII. THE MULTIPLETS.

In a remarkable paper on the analysis of the arc spectrum of manganese Catalán[14] has described a type of regularity to which he has applied the name multiplet. Multiplets are groups of many lines (9, 13, and 15 in the case of manganese) between which not only the frequency differences characteristic of the triplets exist, but in which occur also new differences which are common to the various groups. Catalán includes in his paper three multiplets which belong to the spectrum of chromium. These and other chromium multiplets have recently been announced by Frl. Gieseler.[15]

An explanation of the multiplets of manganese and chromium has recently been given by Sommerfeld[16] on the basis of the quantum theory. Each group of lines may be accounted for by transitions of the valence electron between a polyfold level of one type and another polyfold level of the same or different type. Thus, a 9-line multiplet is regarded as a combination of a fivefold D level with a threefold P level, while a 13-line multiplet may arise from a combination of a fivefold D level with a different fivefold D level. Hence, multiplets are series members as are singlets, doublets, and triplets, and a complete representation of the various energy levels belonging to the atom, of which Figure 1 is only a partial view, would show an array of many complex levels between which the permissible transitions result in the observed spectrum lines.

[14] Phil. Trans. Roy. Soc., London, A 223, p. 146; 1922.
[15] Ann. der Physik. (IV), 70, p. 147; 1922.
[16] Ann. der Physik. (IV), 70, p. 32; 1922.

Multiplets have been found in the spectrum of molybdenum which resemble those found by Catalán for manganese. In the yellow region of the spectrum lies a group of nine lines which are related by frequency differences which characterize the narrow triplets. The following table contains its members, which are all prominent lines:

λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.
6030.66	9	16577.37	5791.86	6	17260.84	5689.22	7	17572.25
5888.32	6	16978.08	5751.41	6	17382.24	5650.14	4	17693.79
5858.28	7	17065.14	5722.78	5	17469.20	5632.48	6	17749.26

Arranging this multiplet to set forth the characteristic differences involved, we have the following scheme:

				17469.20	*404.06*	17065.14	*487.77*	16577.37
				86.96		*87.06*		
		17693.79	*311.55*	17382.24	*404.16*	16978.08		
		121.54		*121.40*				
17749.26	*177.01*	17572.25	*311.41*	17260.84				

Here we have a combination between the triple $2P_i$ level and a new fivefold level, D', between whose components the differences 177.01, 311.48, 404.11, and 487.77 exist. Figure 2 illustrates the relations between the D' levels and some of those with which it combines to produce the multiplets that have been observed. The figure has been drawn to the same scale as Figure 1 and, if superposed on it, would show the maze of levels involved in the production of the observed regularities in the spectrum of molybdenum.

The D' level enters into combination with other levels, as illustrated by the multiplets which follow. The first is a combination between D' and $2p_i$, of which 10 lines have been observed. The members of this multiplet are:

λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.
7391.36	5	13525.60	7060.23	3	14159.95	6934.12	2	14417.47
7267.62	3	13755.88	....	......	[1] 14214.35	6908.23	2	14471.51
7154.15	1	13974.05	6946.71	1	14391.35	6724.89	1	14866.04
7134.09	4	14013.35						

[1] Calculated.

Its arrangement is as follows:

				14866.04				13974.05
				448.57				*448.45*
				14417.47	*404.12*	14013.35	*487.75*	13525.60
				257.52		*257.47*		
		14471.51	*311.56*	14159.95	*404.07*	13755.88		
		257.16						
14391.35	*177.00*	[1] 14214.35						

[1] Calculated.

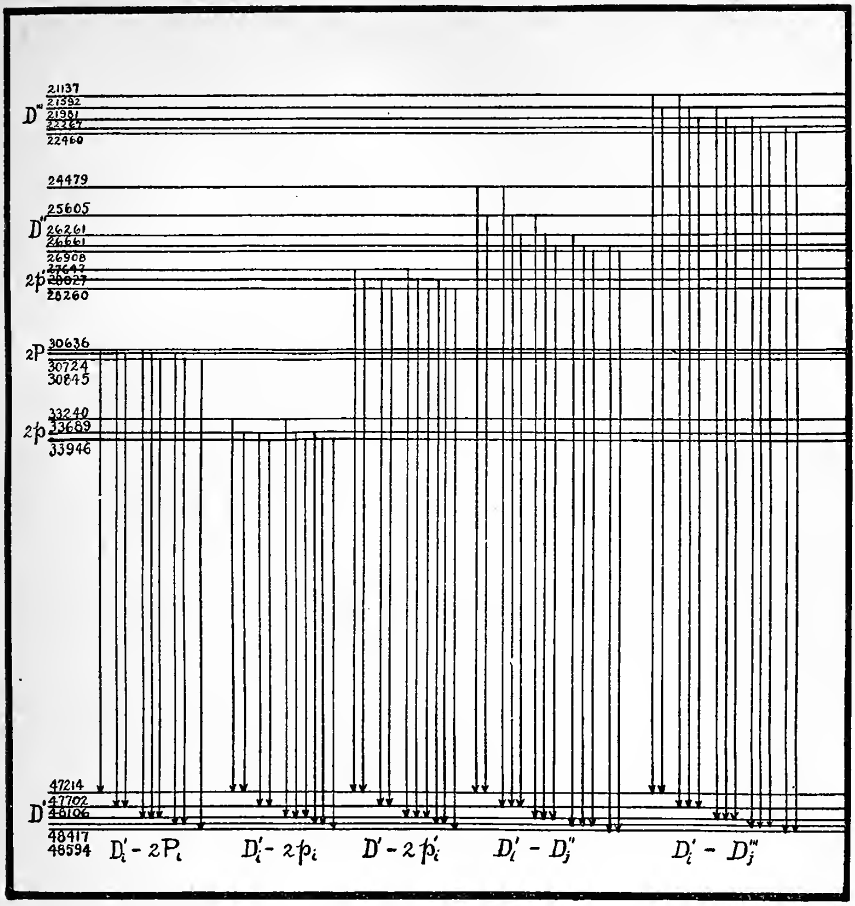

FIG. 2.—*Energy diagram of the multiplets of molybdenum.*

We should expect a similar combination between the D' and $2p'_1$ levels. Adding the quantity $k = 5592.87$ to the wave number 14866.04 gives 20458.91 as the wave number of a corresponding line in a parallel multiplet, whose members were found to be:

λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.
5210.42	2	19186.97	5037.51	1	19845.56	4973.35	2	20101.59
5142.24	1	19441.37	5017.53	1	19924.56	4959.63	1	20157.19
5109.26	1	19566.87	4979.11	5	20078.35	4886.46	3	20459.02
5081.26	2	19674.70						

which is thus arranged:

				20459.02				19566.87
				380.67				*379.90*
				20078.35	*403.65*	19674.70	*487.73*	19186.97
				232.79		*233.33*		
		20157.19	*311.63*	19845.56	*404.19*	19441.37		
		232.63						
20101.59	*177.03*	19924.56						

A 13-line multiplet results from a combination of the D' level with a new fivefold level, say D''. Its members are:

λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.
4662.77	5	21440.50	4595.16	10	21755.97	4512.14	5	22156.25
4661.93	4	21444.36	4576.50	10	21844.65	4443.08	5	22500.63
4647.83	4	21509.40	4558.11	10	21932.81	4397.30	3	22734.86
4626.47	10	21608.73	4524.34	10	22096.52	4304.93	2	23222.65
4609.89	10	21686.42						

Its arrangement is as follows:

						23222.65	*487.79*	22734.86
						1126.13		*1126.13*
				22500.63	*404.11*	22096.52	*487.79*	21608.73
				655.98		*656.02*		
		22156.25	*311.60*	21844.65	*404.15*	21440.50		
		400.28		*400.29*				
21932.81	*176.84*	21755.97	*311.61*	21444.36				
246.39		*246.57*						
21686.42	*177.02*	21509.40						

The separations between the members of the D'' level are 246.48, 400.28, 656.00, and 1126.13. In Figure 2 this group is shown as the combination $D'_i - D''_j$.

Another 13-line multiplet arising from a combination of D' with a fivefold level D''' is as follows:

λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.
3901.78	10	25622.10	3828.88	10	26109.93	3797.31	2	26327.01
3886.82	5	25720.76	3826.70	10	26124.81	3781.60	10	26436.42
3869.08	10	25838.59	3825.33	2	26134.16	3770.52	8	26514.09
3851.40	2	25957.24	3822.99	5	26150.22	3763.36	5	26564.52
3833.76	10	26076.71						

which is thus arranged:

						26564.52	*487.81*	26076.71
						454.59		*454.61*
				26514.09	*404.16*	26109.93	*487.83*	25622.10
				389.28		*389.17*		
		26436.42	*311.61*	26124.81	*404.05*	25720.76		
		286.20		*286.22*				
26327.01	*176.79*	26150.22	*311.63*	25838.59				
192.85		*192.98*						
26134.16	*176.92*	25957.24						

The D''' level is therefore characterized by the separations 192.92, 286.21, 389.22, and 454.60. In Figure 2 this multiplet is illustrated under $D'_i - D'''_j$.

Two groups of lines, each consisting of nine members, lie in the ultra-violet. They both arise from combinations between the D' levels and new levels which are threefold, if the groups are complete as given below. It is possible, however, to find pairs of lines with the separation 488 ± which would give 11 members to each group instead of 9, but it is doubtful whether such an arrangement is correct. The data for the two groups are as follows:

λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.
3461.84*	2	28878.11	3450.81	2	28970.47
3426.79	3	29173.57	3418.52	8	29244.13
3404.35	4	29365.82	3406.01	10	29351.51
3382.29	2	29557.29	3403.35	4	29374.44
3379.97	10	29577.66	3382.49	5	29555.54
3358.13	10	29769.96	3367.64	2	29685.92
3347.02	6	29868.76	3362.37	2	29732.44
3344.75	10	29889.02	3350.31	4	29839.44
3327.31	10	30045.73	3305.56	4	30243.37
3434.79	6	29105.54	3205.88	5	31183.73
3378.20	3	29593.15	3156.51	2	31671.43

The arrangement of these groups is:

						29593.15	*487.61*	29105.54
						227.33		*227.43*
				29769.96	*404.14*	29365.82	*487.71*	28878.11
				192.30		*192.25*		
		29889.02	*311.36*	29577.66	*404.09*	29173.57		
		20.26		*20.37*				
30045.73	*176.97*	29868.76	*311.47*	29557.29				

and:

						31671.43	*487.70*	31183.73
						1831.99		*1832.22*
				30243.37	*403.93*	29839.44	*487.93*	29351.51
				868.93		*868.97*		
		29685.92	*311.48*	29374.44	*403.97*	28970.47		
		130.38		*130.31*				
29732.44	*176.90*	29555.54	*311:41*	29244.13				

Among the fainter lines of the spectrum three groups of seven lines have been found which show recurring frequency differences when properly arranged. Whether or not these groups have a physical significance based on the energy changes within the atom can not be decided as yet. They may be merely numerical coincidences or fragments of groups arising from the interchanges between unknown levels. These groups are presented in the table below:

λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.	λ I. A.	Int.	ν vacuum.
5642.38	2	17718.12	5145.38	4	19429.51	4651.06	3	21494.46
5619.56	2	17790.08	5055.00	2	19776.92	4570.13	5	21875.09
5501.88	5	18170.59	5046.51	2	19810.18	4517.41	3	22130.41
5501.52	3	18171.78	4941.65	3	20230.55	4426.68	5	22583.97
5388.68	2	18552.29	4893.95	2	20427.72	4412.77	3	22655.14
5325.86	1	18771.13	4850.39	1	20611.16	4353.32	3	22964.54
5200.15	4	19224.89	4787.63	2	20881.36	4326.15	10	23108.78

They may be arranged as follows:

		19224.89	*453.76*	18771.13
		1053.11		*1053.01*
18552.29	*380.51*	18171.78	*453.66*	17718.12
381.70		*381.70*		
18170.59	*380.51*	17790.08		

and:

		20881.36	*453.64*	20427.72
		650.81		*650.80*
20611.16	*380.61*	20230.55	*453.63*	19776.92
800.98		*801.04*		
19810.18	*380.67*	19429.51		

and:

		23108.78	*453.64*	22655.14
		524.81		*524.73*
22964.54	*380.57*	22583.97	*453.56*	22130.41
1089.45		*1089.51*		
21875.09	*380.63*	21494.46		

IX. UNCLASSIFIED LINES.

In addition to the results given above, the survey of the spectrum has revealed many pairs and a few triplets of lines between which exist frequency differences that are characteristic of the series triplets and multiplets. It has not been possible so far to classify these lines or to trace their origin to combinations; yet it is not believed that they are to be regarded as merely numerical coincidences.

Perhaps the most prominent pair is one already indicated by Paulson,[17] namely:

λ I. A.	Int.	ν vacuum.	Δν
3158.16 3170.33	5R 10R	31654.89 31533.40	121.49

The second line will be recognized as the series line $1s-(2p_2+k_2)$, and the value of $\Delta\nu$ is that occurring in the series of narrow triplets. Likewise, the middle lines of the diffuse triplet, namely $(2p_2-k)-3d_i$, are paired with other lines by the same frequency difference:

λ I. A.	Int.	ν vacuum.	Δν
7447.30 7515.37	2 1	13423.99 13302.40	121.59
7452.83 7521.00	2 1	13414.03 13292.44	121.59
7456.65 7524.83*	1 <1	13407.16 13285.68	121.48

Each of the other two members of the triplet $1s-(2p_i+k_i)$ is associated with a self-reversed line, thus:

λ I. A.	Int.	ν vacuum.	Δν
3112.12 3132.59	4R 10R	32123.14 31913.20	209.84
3193.97 3208.84	10R 7R	31299.98 31154.98	145.00

but these relationships have not been found repeated elsewhere in the spectrum.

[17] Astrophys Jl., **40**, p. 302; 1914.

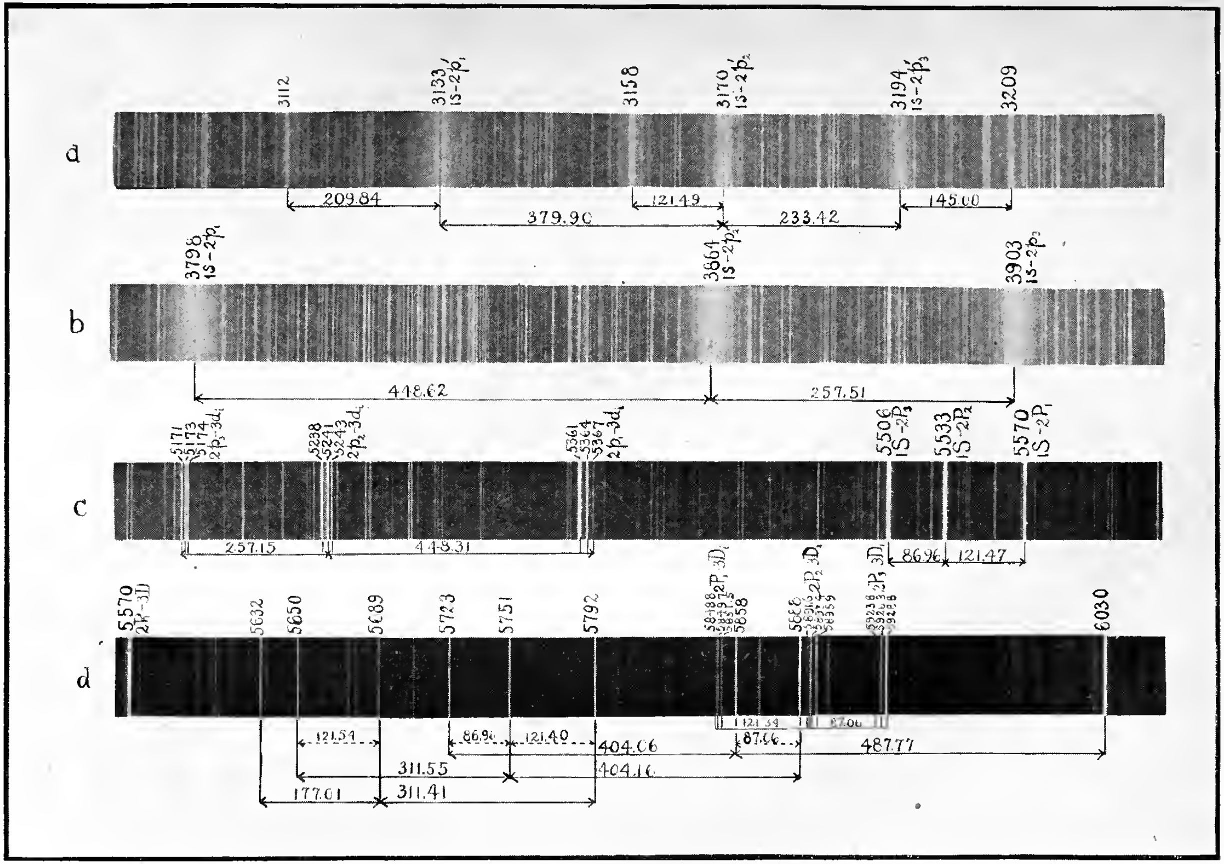

FIG. 3.—*Triplets and multiplet of molybdenum in the regions of shorter wave length.*

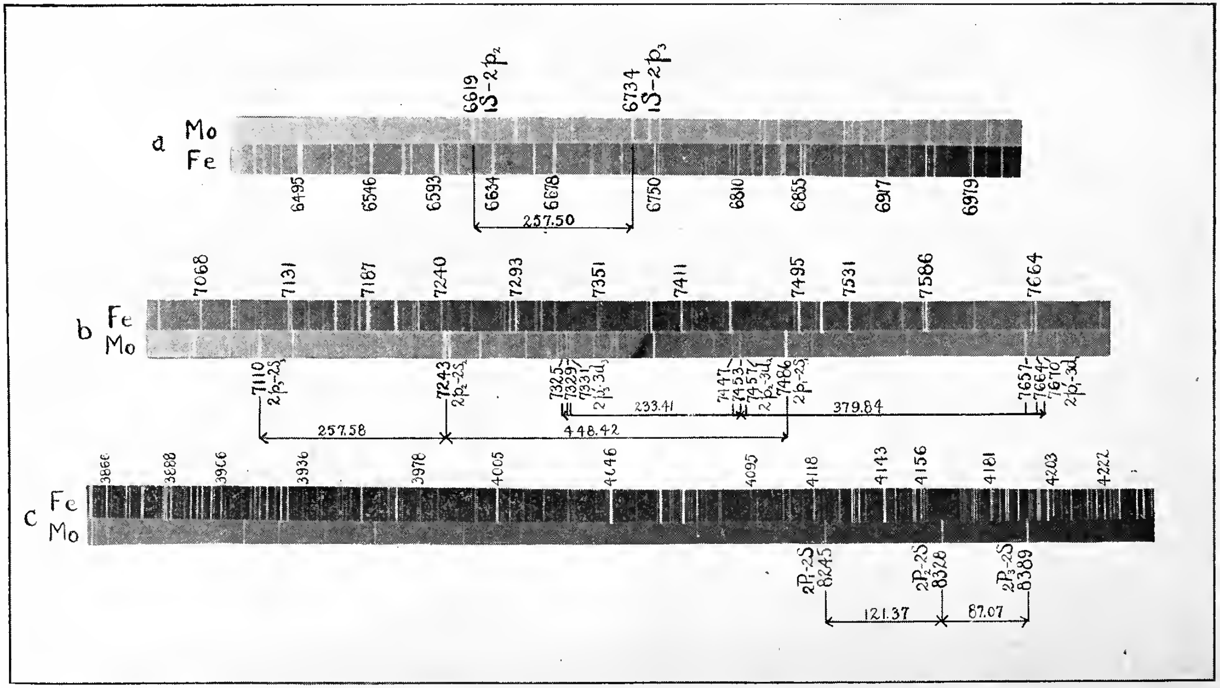

FIG. 4.—*Molybdenum triplets in the red and infra-red spectral regions.*

Other pairs and triplets are brought together in the following table:

λ I. A.	Int.	ν vacuum.	Δν.	λ I. A.	Int.	ν vacuum.	Δν.	λ I. A.	Int.	ν vacuum.	Δν.
5091.35 4977.68	2 2	19635.72 20084.11	448.39	5499.50 5473.36	2 5	18178.44 18265.24	86.80	4369.06 4293.23	5 10	22881.83 23285.98	404.15
4957.53 4849.72	5 5	20165.72 20614.01	448.29	5465.55 5439.68	2 2	18291.37 18378.37	87.00	4105.09 4038.09	5 5	24353.18 24757.26	404.08
4707.26 4609.89	10 10	21237.87 21686.42	448.55	4924.78 4903.80	3 5	20299.83 20386.69	86.86	2972.97 2937.66	2 2	33626.67 34030.85	404.18
4411.71 4326.15	10 10	22660.64 23108.78	448.14	4775.67 4755.89	3 2	20933.64 21020.73	87.09	7413.29 7245.87 7154.15	1 4 1	13485.58 13797.18 13974.05	311.60 176.87
4819.28 4760.21	12 10	20744.22 21001.61	257.39	4719.77 4700.49	2 2	21181.54 21268.45	86.91	3518.22 3480.10	2 2	28415.39 28726.63	311.24
7748.93 7676.63	1 1	12901.46 13022.97	121.51	4517.14 4499.45	6 2	22131.73 22218.72	86.99	3517.55 3479.43	2 3	28420.80 28732.16	311.36
5475.89 5439.68	5 2	18256.81 18378.37	121.56	4293.23 4277.25	10 12	23285.98 23372.95	86.97	3434.05 3397.69	10 3	29111.82 29423.36	311.54
5450.51 5414.63	4 2	18341.82 18463.37	121.55	4084.39 4069.89	10 8	24476.63 24563.81	87.18	3382.29 3347.02	2 6	29557.38 29868.76	311.38
4814.47 4786.47	2 3	20764.94 20886.42	121.48	3614.25 3602.94	10 5	27660.37 27747.26	86.89	6407.67 6335.75	2 2	15601.98 15779.09	177.11
3680.69 3664.31	5 2	27161.15 27282.52	121.37	3193.97 3185.10	10 5	31299.98 31387.22	87.24	4446.43 4411.71	2 10	22483.68 22660.64	176.96
3629.31 3613.38	3 2	27545.63 27667.03	121.40	4397.30 4304.93	3 2	22734.87 23222.65	487.78	4066.38 4037.31	3 2	24585.01 24762.04	177.03
9424.69 9348.01	1 2	10607.52 10694.54	87.02	4380.30 4288.65	3 5	22823.13 23310.84	487.71	4057.60 4028.65	3 5	24638.19 24815.25	177.06
7854.44 7801.12	2 1	12728.15 12815.16	87.01	3626.19 3563.14	5 5	27569.33 28057.18	487.85	3459.92 3438.87	3 5	28894.14 29071.04	176.90
7088.78 7045.29	2 2	14102.92 14189.97	87.05	3508.12 3449.08	5 5	28497.18 28985.01	487.83	3304.23 3285.03	3 5	30255.54 30432.41	176.87
5884.32 5854.36	2 1	16989.61 17076.56	86.95	3493.34 3434.79 3387.75	2 6 4	28617.71 29105.55 29509.67	487.84 404.12	2945.67 2930.40	3 2	33938.23 34115.14	176.91
5583.28 5556.27	3 4	17905.68 17992.70	87.02	3441.45 3384.62	5 10	29049.08 29536.95	487.87				

X. THE ILLUSTRATIONS.

Figures 3 and 4 were prepared to illustrate some of the prominent lines of the arc spectrum of molybdenum which have been classified. In Figure 3, *a* and *b*, are fourfold enlargements from spectrograms made in the second order of the 20,000-lines-per-inch grating and illustrate the two intense, self-reversed triplets which constitute the groups $1s-2p_i$ and $1s-(2p_i+k_i)$. Of particular interest is the association of the latter triplet with three other strong, self-reversed lines of wave lengths 3112 A, 3158 A, and 3209 A. As has already been indicated, the frequency difference between 3158 A and 3170 A is 121.49, which is the larger frequency difference occurring in the narrow triplets. In Figure 3, *c*, are shown the diffuse triplet $2p_i-3d_j$ and the triplet $1S-2P_i$. Of

particular note is the fact that the intensity of 5570 A is less than the intensities of the two other members of the triplet. Two groups, each consisting of nine lines, are illustrated in *d*. The first one is the diffuse triplet $2P_i - 3D_i$; the second is a multiplet which brings into prominence the frequency differences 488, 404, 311, and 177, which appear in other multiplets. Both *c* and *d* are enlarged 2.5 times from spectrograms made in the second order of the 7,500-lines-per-inch grating.

Figure 4 illustrates portions of the spectrum which were observed in the regions of longer wave length with the first order of the 7,500-lines-per-inch grating. Each of the three illustrations has been enlarged about threefold from the original negatives. In *a* and *b* the first order spectrum of iron is juxtaposed to that of molybdenum, and in *c* appears the second order iron spectrum with the molybdenum spectrum. In *a* are shown the interseries combination lines $1S - 2p_i$. The wide triplet of the sharp series, $2p_i - 2s$ and the diffuse triplet $(2p_i - k_i) - 3d_j$, are shown in *b*. In *c* appears the narrow triplet $2P_i - 2S$, of which the first line is less intense than the other two.

XI. CONCLUSION.

The published tables of wave lengths contain a total of about 3,300 lines for the arc spectum of molybdenum. Of these about 150, or fewer than 5 per cent, have been classified as belonging to series triplets and multiplets. Forty of the classified lines are entered in the tables as of intensity 7 or greater, as compared with a total of 90 lines for the entire observed spectrum within the same range of intensities. The great majority of molybdenum lines are faint; that is, of intensities 1 or 2. That the fainter lines must also be considered in unraveling a spectrum is evidenced by the fact that nearly all of the complex triplets and multiplets described above contain lines of intensities 1 and 2. A complete accounting of all the lines in the spectrum as resulting from interorbital transitions of the valence electron of the atom would lead to a very complicated system of orbits or energy levels of which Figures 1 and 2 are only partial views.

Various aids in the analysis of spectra are seen in the Zeeman effect, the Stark effect, and the temperature classification of spectrum lines. That other modes of describing the characteristics of lines, such as pressure shifts, reversibility, etc., would be helpful is recognized; but it is of interest to note that very few

data of the types mentioned are available for molybdenum. Jack [18] has studied the Zeeman effect for molybdenum, and has given the types of resolution for many lines. Four lines of the same Zeeman pattern have been arranged into a series by him, but the series does not satisfy a formula of the Ritz type, nor do the members of his series belong to any of the triplets or multiplets described in this paper. Indeed, very few of the lines which are members of triplets and multiplets and which have been studied by Jack are of the same Zeeman pattern.

Even though qualitative aids may play an important part in the interpretation of a line spectrum, the ultimate test of the correctness of series and other relationships between lines must be found in recurring constant frequency differences. These quantities are derived directly from measured wave lengths which are the fundamental data of spectroscopy. In view of the growing importance of spectrum regularities in modern physics, it would be desirable to publish the wave numbers of lines as well as wave lengths in tables of spectroscopic data.[19]

WASHINGTON, April 27, 1923.

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[18] Ann. der Physik. (IV), 28, p. 1032; 1909.

[19] Since this article was put in type, a paper by Catalán on the same subject has arrived, too late for consideration in the text. See Anales Españ. de Fís. y Quím., 21, p. 213; 1923.